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Application for examination according to ☐ 44 Patent Law has been made.

(54) Melt-spun, crosslinked elastic threads of polyethylene and processes for manufacturing and using them

(57) The invention pertains to the areas of chemistry and textile technology and pertains to threads of polyethylene, which can be used for example for textiles and non-woven materials.

The goal of the invention consists of improving the thermal stability and the elastic restoring capacity of melt-spun threads.

The goal is achieved by melt-spun crosslinked elastic threads of polyethylene with defined side chain structure and a narrow molecular weight distribution of $M_w/M_n \leq 2.2$, in which by hydrolysis of the functionalized organosilane grafted onto the polyethylene chains and/or side chains and by polycondensation from the silanols produced from them between the polyethylene chains and/or side chains, a crosslinking is present over Si-O-Si bridges and by a process for producing such threads.

The statements that follow were taken from documents submitted by the applicant.

Specification

The invention pertains to the areas of chemistry and textile engineering and involves melt-spun, crosslinked elastic threads made of polyethylene, as can be used for example for textiles and nonwoven materials and a process for producing such threads as well as their use.

Threads with elastomeric properties made from polyurethanes have long been known. Such filaments are also known as elastan yarns. They are made with solvent and/or melt spinning processes. The manufacturing and the properties of such threads were described in detail by M. Fabricius, among other things, in "Elastane fibers (Spandex)", *Chemical Fibers International*, October 1995, pages 400-410.

One drawback with these threads is that they are usually produced in solvent-spinning processes and that essentially toxic chain extenders must be used. In addition, in this process a high engineering and energy expenditure is necessary for solvent recovery, treating the vapors produced, work-up of the spinning solutions produced, and disposing of the waste products. Another particular drawback is that the melt-spun thermoplastic polyurethane threads after spinning must be subjected to tempering treatment for many hours on the spool for complete structural development.

Not much is known to date about non-crosslinked fibers with elastomeric properties made of polyethylenes. In WO 94/125647, the melt spinning of elastomeric threads made of a polyethylene with defined side chain structure and a narrow molecular weight distribution of $M_w/M_n \leq 2.2$ is described. For these threads an elastic recovery of more than 50% at 100% elongation is specified. The elastic properties of these threads result from the defined side chain structure of the polyethylene.

In WO 94/125648 the melt spinning of the same material is described, as well as the use of these threads for commercial purposes, for example for disposable diapers.

Wang, Li et al. in *J. Polym. Mater.* (1993); 10(1): pages 57-60 describe the synthesis of ethylene/propylene block copolymers and their use for producing hard elastic threads. In contrast to the polyethylene threads described, these threads have a different main chain and side chain structure and therefore have only slight extension capabilities.

The drawback of the known melt-spun threads made of polyethylene with a defined side chain structure and a narrow molecular weight distribution of $M_w/M_n \leq 2.2$ consists of the fact that they have a low crystallite melt temperature of about 60°C, which is too low if threads for the usual technical and textile applications are to be produced from them.

The goal of the invention consists of improving the thermal stability and the elastic restoring capacity of melt-spun threads of polyethylene with a defined side chain structure and a narrow molecular weight distribution of $M_w/M_n \leq 2.2$.

The goal is accomplished by the invention indicated in the claims.

In accordance with the invention, in the case of the melt-spun, crosslinked, elastic threads made of polyethylene with a defined side chain structure and a narrow molecular weight distribution of $M_w/M_n \leq 2.2$ by hydrolysis of the functionalized organosilanes grafted onto the polyethylene chains and/or side chains and by polycondensation from the silanols produced in this way, between the polyethylene chains and/or side chains a crosslinking over SI-O-SI bridges is present.

Advantageously the functionalized organosilanes are alkoxyvinyl silanes.

Also advantageously, in the case of the melt-spun crosslinked elastic threads made of polyethylene with defined side chain structure and a narrow molecular weight distribution of $M_w/M_n \leq 2.2$ in accordance with the invention, the gel content, as degree of crosslinking, is ≥ 55 wt%.

Furthermore, the goal is accomplished in accordance with the invention by a process for producing melt-spun, crosslinked elastic threads from polyethylene with defined side chain structure and a narrow molecular weight distribution of $M_w/M_n \leq 2.2$, in which before the melt-spinning the polyethylene with defined side chain structure and a narrow molecular weight distribution of $M_w/M_n \leq 2.2$ is treated with one or more free radical initiators, and a functionalized organosilane or a mixture thereof is grafted in a free radical way onto the polyethylene chain(s) and/or side chain(s) and in which before and/or after the grafting a plasticizer oil is added, and in which after the subsequent melt spinning, the hydrolysis of the functionalized organosilanes grafted onto the polyethylene chains and/or side chains and polycondensation of the silanols produced in this way is carried out.

Advantageously the treatment with free radical initiators and the grafting with functionalized organosilanes is performed in an extruder.

Also advantageously as functionalized organosilanes alkoxyvinylsilane, such as vinyltriethoxysilane or vinyltrimethoxysilane, are used.

Likewise advantageously as a free radical initiator organic peroxide with a high fraction of active oxygen is used.

It is also advantageous that 15-30 wt% plasticizer oil are added.

It is also advantageous that paraffin oil is used as plasticizer oil.

It is likewise advantageous that the hydrolysis of the functionalized organosilanes grafted onto the polyethylene chains and/or side chains and the polycondensation of the silanols produced in this way are performed by aqueous preparation or by humidity from the air.

It is also advantageous that the hydrolysis of the functionalized organosilanes grafted onto the polyethylene chains and/or side chains and the polycondensation of the silanols produced in this way are performed immediately after the melt spinning process.

And it is also advantageous that the hydrolysis of the functionalized organosilanes grafted onto the polyethylene chains and/or side chains and the polycondensation of the silanols produced in this way are only performed after a further processing of the polyethylene threads produced by melt spinning.

The melt-spun, crosslinked elastic threads of polyethylene with a defined side chain structure and a narrow molecular weight distribution of $M_w/M_n \leq 2.2$ produced in accordance with the invention are used in accordance with the invention for producing nonwoven materials prepared according to the spun nonwoven or melt-blown process.

Advantageously the melt-spun, crosslinked elastic threads made of polyethylene with a defined side chain structure and a narrow molecular weight distribution of $M_w/M_n \leq 2.2$ produced in accordance with the invention are used for mechanically, thermally, or chemically consolidated nonwoven materials in which the hydrolysis of the functionalized organosilane grafted onto the polyethylene chains and/or side chains and the polycondensation of the silanols produced in this way have taken place before, during, or after the consolidation of the nonwovens.

As a result of the process in accordance with the invention, before the melt-spinning of polyethylenes with a defined side chain structure known in and of itself and a molecular weight distribution $M_w/M_n \leq 2.2$, advantageously in an extruder, the polyethylene is mixed with a free radical initiator, preferably an organic peroxide with a high fraction of active oxygen, and with functionalized organosilane, advantageously alkoxyvinylsilanes. In this process the functionalized organosilanes are grafted in a free radical manner to the polyethylene chains and/or side chains. To this mixture before and/or after grafting a plasticizer oil, preferably 15-30 wt% of a paraffin oil, are added. This plasticizer oil serves for lowering the melt viscosity and thus improves the processing properties of the grafted polyethylene during melt spinning and reduces the Shore hardness of the thread produced. On the threads produced, either before winding on a device an aqueous preparation is applied, which leads to hydrolysis of the functionalized organosilanes grafted onto the polyethylene chains and/or side chains and the polycondensation of the silanols produced in this way and thus to crosslinking of the thread over Si-O-Si bridges, or the hydrolysis of the functionalized organosilanes grafted onto the polyethylene chains and/or

side chains and the polycondensation of the silanols produced in this way are performed at a later time.[??]

Since the thread on the device, as a rule a spinning reel, is subjected to a molding tension, no additional technical measures are necessary for fixing the geometry during the hydrolysis of the functionalized organosilanes grafted onto the polyethylene chains and/or side chains and the polycondensation of the silanols produced in this way, leading to crosslinking of the thread.

The threads produced in accordance with the invention show, as a result of their crosslinking, a considerably improved thermal stability and are still stable in shape even at temperatures of 100°C.

The solution in accordance with the invention can also be used for producing elastomeric nonwoven materials, preferably according to the spun-web or melt-blown process. In this case the hydrolysis of the functionalized organosilanes grafted onto the polyethylene chains and/or side chains and the polycondensation of the silanols produced in this way is achievable by the water contact for crosslinking on the spun filaments or fibers initially laid out water-free on the nonwoven strip, depending on the desired consolidation manner, is accomplished before (mechanical consolidation), after (mechanical or thermal consolidation) or coupled with a consolidation agent (chemical consolidation) by wetting or saturating the nonwoven strip.

In the following, the invention will be explained based on an exemplified embodiment.

A mixture is produced from 35 g polyethylene (ENGAGE EG 8200 (Dow Chemical Company)), 1.12 g vinyltriethoxysilane, 0.056 g dihydroxybutyl peroxide, 8.75 g medical white oil DAB 9, subl. P 2071 and 0.007 g dibutyl tin dilaurate in a laboratory kneader at 120°C and 30 rpm within 5 min. Then the temperature is raised to 180°C and the rotation speed reduced to 20 rpm. The measured rotational momentum on the laboratory kneader after 3 min clearly shows the beginning of chain activation and the free radical grafting of the silane onto the polyethylene at about 175°C. In this process the mixing chamber of the laboratory kneader is constantly purged with nitrogen. The sampling takes place under nitrogen purging, and the intermediate storage in a desiccator over the drying agent phosphorus pentoxide. Then the sample is melted in a small spinning unit with piston extrusion and winding device, spun at 250°C, and wound up with a final velocity of 25 m/min. The initiation of the crosslinking by hydrolysis of the vinyltriethoxysilane grafted onto the polyethylene chains and/or side chains and the polycondensation of the silanols produced in this way takes place by wetting the thread with an aqueous spinning preparation about 50 cm below the spinning nozzle. To accelerate the crosslinking, the thread on the reel was additionally moistened with atomized water.

A melt produced in this way can be spun well. The thread can be unwound from the reel without any sticking after crosslinking.

The gel content is determined on another sample of the above-described batch after it has been treated in boiling water. The determination of the gel content was performed by a 20-hour hot extraction in a Kuhlmann attachment with boiling xylene.

In this process a gel content of 63.2 wt% was determined.

The tensile testing takes place with a clamping length of 50 mm and a testing speed of 250 mm/min. The physical breaking tension of the filaments [*threads?*] not yet crosslinked is 2.13 cN/dtex. After crosslinking a value of 2.98 cN/dtex was measured.

The elastomeric behavior was determined by alternating extension loading in a tensile testing device. In this process a 100 mm long thread was extended in three cycles with a test speed of 500 mm/min to 300% and relaxed to 0% extension. The value of the elastic recovery after the third elongation cycle for the non-crosslinked threads was 60.3%, and for the crosslinked threads 72.2%, based on 300% elongation length.

In the thermal mechanical analysis (TMA) a thread with a clamping length of 13 mm was tested. The thread was clamped with a mechanical prestress of 0.0 to 5 cN/dtex and heated above 30°C at 10 K/min. The relative change in length was measured as a function of the temperature and shown graphically (Figure 1).

Claims

1. Melt-spun, crosslinked elastic threads made of polyethylene with defined side chain structure and a narrow molecular weight distribution of $M_w/M_n \leq 2.2$ in which, by hydrolysis of the functionalized organosilanes grafted onto the polyethylene chains and/or side chains and by polycondensation of the silanols produced in this way a crosslinking over Si-O-Si bridges is present between the polyethylene chains and/or side chains.
2. Melt-spun, crosslinked elastic threads made of polyethylene in accordance with Claim 1, in which the functionalized organosilanes are alkoxyvinylsilanes.
3. Melt-spun, crosslinked elastic threads made of polyethylene in accordance with Claim 1, in which the gel content as degree of crosslinking amounts to ≥ 55 wt%.
4. Process for producing melt-spun, crosslinked elastic threads from polyethylene with a defined side chain structure and a narrow molecular weight distribution of $M_w/M_n \leq 2.2$, in which before the melt-spinning the polyethylene with a defined side chain structure and a narrow molecular weight distribution of $M_w/M_n \leq 2.2$ is treated with one or more free radical initiators and a functionalized organosilane or a mixture thereof is subjected to free radical grafting onto the polyethylene chain(s) and/or side chain(s) and

in which before and/or after the grafting a plasticizer oil is added and in which after the subsequent melt-spinning the hydrolysis of the functionalized organosilanes grafted onto the polyethylene chains and/or side chains and the polycondensation of the silanols produced in this way is carried out.

5. Process in accordance with Claim 4, in which the treatment with free radical initiators and the grafting with functionalized organosilanes is performed in an extruder.

6. Process in accordance with Claim 4, in which as the functionalized organosilanes alkoxyvinylsilane such as vinyltriethoxysilane or vinyltrimethoxysilane is used.

7. Process in accordance with Claim 4, in which as the free radical initiator organic peroxide with a high fraction of active oxygen is used.

8. Process in accordance with Claim 4, in which 15-30 wt% plasticizer oil are added.

9. Process in accordance with Claim 4, in which paraffin oil is used as the plasticizer oil.

10. Process in accordance with Claim 4, in which the hydrolysis of the functionalized organosilanes grafted onto the polyethylene chains and/or side chains and the polycondensation of the silanols produced in this way is performed by aqueous preparation or by the humidity from the air.

11. Process in accordance with Claim 4, in which the hydrolysis of the functionalized organosilanes grafted onto the polyethylene chains and/or side chains and the polycondensation of the silanols produced in this way is performed immediately after the melt-spinning process.

12. Process in accordance with Claim 4, in which the hydrolysis of the functionalized organosilanes grafted onto the polyethylene chains and/or side chains and the polycondensation of the silanols produced in this way is only carried out after a further processing of the polyethylene threads produced by melt-spinning.

13. Use of a melt-spun, crosslinked elastic polyethylene thread with defined side chain structure and a narrow molecular weight distribution of $M_w/M_n \leq 2.2$, in which crosslinking of the polyethylene chains and/or side chains over Si-O-Si bridges is present, for nonwoven materials produced by nonwoven spinning or melt-blown processes.

14. Use of a melt-spun, crosslinked elastic fiber [*thread?*] of polyethylene according to Claim 13, in which the nonwoven materials are consolidated mechanically, thermally, or chemically and the hydrolysis of the organosilanes grafted onto the polyethylene chains and/or side chains and the polycondensation of the silanols produced in this way takes place before, during, or after the consolidation of the nonwovens.

One page of drawings attached.

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Figure 1

[KEY: left: Relative change in length in %; at bottom: Temperature in °C; box in figure: non-crosslinked, crosslinked]

